# Theoretical Studies on the Hydrogen Atom Transfer Reaction (II)*

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The hydrogen atom transfer reaction between substituted methane, $CH_3X$, and its radical, $CH_2X(X = H, F, CH_3, CN, OH$ and $NH_2)$ was studied by MINDO/3 method. The transition state(TS) structure and energy barriers were determined and variation of the transition state and of the reactivity due to the change of X were analyzed based on the potential energy surface characteristics. It was found that the greater the radical stabilization energy, the looser the TS becomes; the TS occurs at about 15% stretch of the C-H bond, which becomes longer as the radical stabilization energy of $CH_2X$ increases. The intrinsic barrier, $\Delta E^*_{X,X}$, of the reaction with X was found to increase in the order $H<F<CH_3<CN<OH<NH_2$. The degree of bond stretch of the C-H bond at the TS also had the same order indicating that the homolytic bond cleavage of the C-H bond is rate-determining. Orbital interactions at the TS between LUMO of the fragment C---H---C and the symmetry adapted pair of nonbonding, $n\pm(=n_1\pm n_2)$, or pi orbitals of the two X atoms were shown to be the dominant contribution in determining tightness or looseness of the TS. The Marcus equation was shown to apply to the MINDO/3 barriers and energy changes of the reaction.

## Introduction

Extensive work has been directed to correlate reactivities and transition-state structures of an organic reaction with substituent variation.[1] Recently various models for interpreting such correlation have been proposed based on the Bell-Evans-Polanyi[2] and Hammond[3] principles. More O'Ferrall plots[4] have provided one of the most useful potential energy surface(PES) model, and seen increasing use for qualitative interpretation of substituents effects on transition state(TS) variations in a wide variety of reactions. On the other hand Marcus theory[5] has provided a simple picture of how thermodynamic and kinetic substituent effects combine to affect the overall barriers to various types of reactions including electron-transfer reaction,[6] proton-transfer[7] and alkyl-transfer reaction in solution,[8] and gas-phase ion-molecule reaction.[9]

In this work we extend our theoretical investigation on the hydrogen atom transfer(HAT) reaction[10]; we have dealt with the HAT from methyl amine to methyl radical and that involving the symmetric transfer reaction(1).

$$XCH_3 + CH_2Y \rightarrow CH_2X + YCH_3 \qquad (1)$$
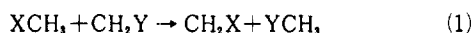
where $X = Y = H, F, OH, CN, CH_3$, and $NH_2$.

We have discussed TS variations with the substituent change using the PES model and applied Marcus theory to our results.

## Calculation

For closed shell ground states and radicals MINDO/3-RHF and -UHF method[11] were used, respectively, in geometry optimization with respect to all geometrical parameters.

In the TS determination for the HAT between methyl amine and methyl radical, the distance between the H Atom being transferred(H*) and the radical carbon was taken as reaction

coordinate and a classical method[12] of TS location was used.

In the symmetric transfer reaction(1), all geometrical parameters were optimized under the symmetry condition $(X = Y = H(D_{3h}), OH(C_i), F, NH_2, CN, CH_3(C_{2h}))$ since a symmetric TS structure can be assumed for such a reaction.[13]

In all cases, the TS structure was characterized by minimization of gradient norm and confirming that there is only one negative eigenvalue in Hessian matrix.[14]

## Results and Discussion

The most stable structures for methyl amine and methyl amine radical are shown in Figure 1. Inspection of this Figure reveals that the structure of methyl amine radical corresponds to a structure in which three-electron interaction is most efficient; as a result the C-N bond length decreases substantially (by 0.09 Å) in contrast to a small decrease in the C-H bond length (by 0.02 Å) as the carbon hybridization changes from $sp^3$ to $sp^2$ in the course of methyl amine radical formation from methyl amine.

The angle formed between the C-N bond axis and the line bisecting HNH on the $NH_2$ plane is much smaller for methyl amine radical than that for methyl amine. This seems to originate from more efficient orbital interaction of the two nonbonding orbitals due to energy gap narrowing that results from elevation of the lone pair orbital level by increasing p orbital character of $NH_2$ and depression of $CH_2$ orbital level by pyramidalization and hence increasing s character.
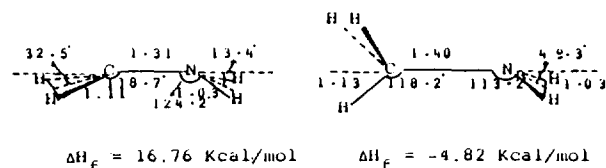


$$\Delta H_f = 16.76 \text{ Kcal/mol} \qquad \Delta H_f = -4.82 \text{ Kcal/mol}$$

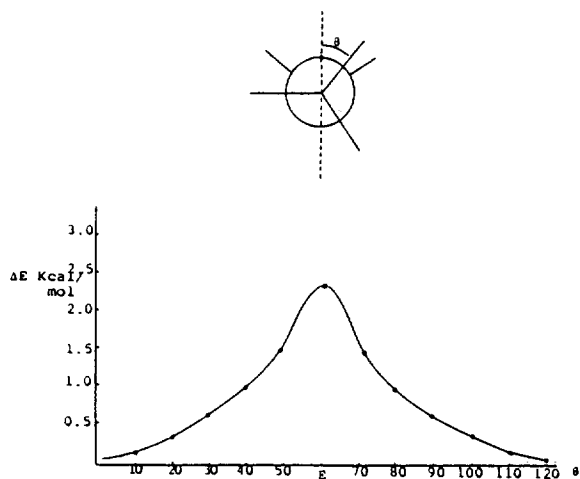**Figure 1.** Structures and heats of formation for methyl amine and methyl amine radical.

**Figure 2.** Rotational barrier (rigid) of methyl amine E; Eclipsed form, in which the lone pair on N atom and a methyl hydrogen overlap completely.
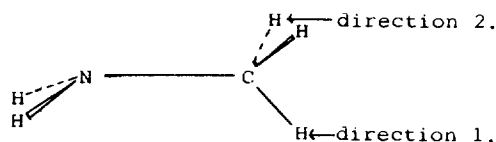


**Figure 3.** Two directions of attack (reaction paths) on hydrogens of methyl amine.
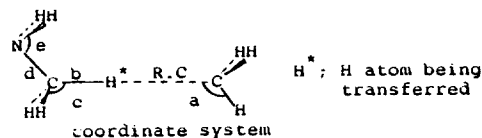
The rigid rotational barrier of methyl amine is shown in Figure 2.

Staggered form is seen to be the most stable one and the height of barrier corresponding to the energy gap between staggered and eclipsed form is 2.36 Kcal/mol. Methyl amine is thus considered to exist predominantly in the staggered form. For this structure we can think of two directions of attack in HAT reaction, path 1 and 2, as shown in Figure 3.

The coordinate system and changes in energy and structure with the reaction coordinate(RC) in vicinity of the TS are summarized in Tables 1 and 2 for the paths 1 and 2 respectively.

Reference to these Tables show that variations in energy and geometric parameters within the range investigated are continuous; the maxima obtained can be taken as the true TS as Rothman and Lohr[16] have claimed. Inspection of Table 2 shows that dihedral angles of the two amine hydrogens(HNCH*) in the path 2 remain practically constant at ~60 and ~180 for the RC change from 1.70 Å to 1.50 Å(RC) but change to ~60 and ~300 at about RC = 1.40 Å. The energy and structure at this point become identical with those for the corresponding species in path 1 (Table 1). This shows that the two attacking modes coalesce to a common species after passing through separate reaction path and different TS.

Another interesting aspect of this reaction is that although considerations of the principle of least motion[17] and the stabiliz-



coordinate system

H* ; H atom being transferred

**TABLE 1: Changes in Energy and Structure with the Reaction Coordinate (RC) for Path 1**

| R.C | 1.85 | 1.75 | 1.70 | 1.67* | 1.65 | 1.60 | 1.55 | 1.50 | 1.45 |
|---|---|---|---|---|---|---|---|---|---|
| E* | 40.15 | 40.36 | 40.42 | 40.42 | 40.42 | 40.38 | 40.27 | 40.07 | 39.71 |
| a** | 103.2 | 103.9 | .104.3 | 104.5 | 104.8 | 105.3 | 105.7 | 106.3 | 106.3 |
| b⁺⁺ | 1.14 | 1.15 | 1.15 | 1.16 | 1.16 | 1.17 | 1.18 | 1.19 | 1.19 |
| c** | 104.3 | 104.2 | 104.0 | 104.0 | 103.9 | 103.6 | 103.5 | 103.4 | 103.4 |
| d⁺⁺ | 1.40 | 1.39 | 1.39 | 1.39 | 1.39 | 1.39 | 1.39 | 1.39 | 1.39 |
| e | 113.6 | 114.2 | 114.5 | 114.0 | 114.6 | 114.6 | 114.6 | 114.8 | 114.8 |

* in Kcal/mol. ** in degree. ⁺⁺ in A. ⁺ The point corresponding to the TS characterized by gradient norm minimization and single negative eigenvalue in the Hessian matrix.
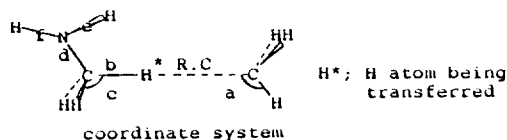


coordinate system

H* ; H atom being transferred

**TABLE 2: Changes in Energy and Structure with the Reaction Coordinate (RC) for Path 2**

| R.C | 1.70 | 1.60 | 1.55 | 1.50 | 1.50* | 1.48 | 1.45 | 1.40 |
|---|---|---|---|---|---|---|---|---|
| E* | 41.09 | 41.34 | 41.47 | 41.47 | 41.47 | 41.47 | 41.35 | 39.03 |
| a** | 104.1 | 105.0 | 105.9 | 105.9 | 105.8 | 106.2 | 106.5 | 107.4 |
| b⁺⁺ | 1.15 | 1.16 | 1.18 | 1.18 | 1.18 | 1.18 | 1.20 | 1.26 |
| c** | 104.8 | 104.6 | 104.1 | 104.1 | 103.2# / 105.2 | 104.2 | 103.7 | 102.7 |
| d⁺⁺ | 1.40 | 1.40 | 1.40 | 1.40 | 1.39 | 1.40 | 1.39 | 1.37 |
| ᵉe** | 68.4 | 68.4 | 68.4 | 68.4 | 72.1 | 68.6 | 77.4 | 64.3 |
| ᵉf** | 189.0 | 189.2 | 189.1 | 189.1 | 193.9 | 189.3 | 200.0 | 293.9 |

* in Kcal/mol. ** in degree. ⁺⁺ in A. ⁺ The point corresponding to the TS characterized by gradient norm minimization and single negative eigenvalue in the Hessian matrix. ᵉ Two different values for the two H atoms. # HNCH* dihedral angle.

ing effect of three-electron interaction arising in the methyl amine radical as hydrogen atom is detached may seem to favor the path 2 relative to the path 1, activation energy is actually lower for the path 1 by 1 Kcal/mol. The following rationalization may account for this apparent inconsistency: (1) The stabilizing three-electron interaction actually occurs in the methyl amine radical but the radical formation is not yet complete at the TS of the path 2, since the TS is relatively early along the reaction coordinate and HAT is in its early stage. (2) In the reaction path 1. $n-\sigma^*$ interaction[18] between the lone pair orbital on the N atom($n_N$) and $\sigma^*$ orbital of the antiperiplanar $C-H^*$ bond is strong so that weakening of he $C-H^*$ bond lowers that activation energy. That the $n-\sigma^*$ interaction is indeed significant is shown by the loose *i.e.*, elongated $C-H^*$ bond relative to other C-H bonds in the structure of methyl amine in Figure 1.

It can be seen in Tables 1 and 2 that in both reaction paths the bond breaking(b) is much less than the bond forming(RC) at the TS indicating that the TS is relatively early along the reaction coordinate. Energy barriers for the symmetric transfer reaction (1), $\Delta E^*_{X,X}$, energy change of the reaction, $\Delta E_{X,H}$, and energy barrier, $\Delta E^*_{X,H}$, with $X \neq Y = H$ in eq(1) determined in this work are summarized in Table 3, together with the effect of group(Y) substitution on the stabilization energy of free radical $CH_2Y$ expressed in terms of the decrease($\Delta E_s$) in homolytic bond dissociation energy, D(R-H), with respect to the reference value D(CH₃H).

Activation energy of the symmetric transfer reaction with X, $\Delta E^*_{X,X}$, increases in the order H<F<CH₃<CN<OH<NH₂, which is exactly the order of radical stabilization energy, $\Delta E_s$; the more is radical stabilized, the more difficult will be to disrupt the radical state. It is considered due to greater stabilizing effect in reactants than in transition states. Approximate linearity found in Figure 4 between $\Delta E_s$ and $\Delta E^*_{X,X}$ is in accord with the contention of Pross *et. al.*,[19] that theoretically effect of substituent should be linearly correlated with the stabilization of reaction complex.

Since the reaction is exothermic, *i.e.*, $\Delta E_{X,H} < 0$, and the TS is an early type, the Hammond postulate is satisfied for the reaction 1 with $X \neq Y = H$. The activation energy for the more exothermic reaction(X = NH₂) is lower than that for the less exothermic one(X = H) in accordance with the Bell-Evans-

Polanyi relation.

The C-H bond lengths for closed shell reactant molecules, $d$, and for the TS, $d^*$, in the symmetric transfer reaction are shown in Table 4. The Table shows that the C-H bond stretch at the TS is about 15% of that in a neutral molecule and for a substituted methane(X≠H) the degree of bond-stretch in the TS formation, $\Delta d$, is greater than that for the unsubstituted (X = H) one. The TS variation with $\Delta d$ can be conveniently illustrated using the PES diagram shown in Figure 5. Since it has been shown that the TS is symmetric for the symmetric transfer reaction (1), the TS should lie along the diagonal line AD. Moreover since the point D is higher than the point A and the TS is a minimum point along the line AD, the location of the TS will be nearer to the associated form, A. *i.e.*, the TS is relatively tight. Since $\Delta E_s$ values in Table 4 are greater for substituted radicals *i.e.*, the radical ·CH₂X is stabilized more than ·CH₃, it is evident that the corner D will be depressed by substitution and the TS location will shift toward the corner D along the diagonal line AD in accordance with the anti-Hammond rule; the TS will thus become looser, *i.e.*, $\Delta d$ will increase with substitution(X≠H).

Variation of transition state structure may be rationalized with orbital interaction scheme shown in Figure 6. The TS is partitioned into two fragments A and B; A is formed by linear com-
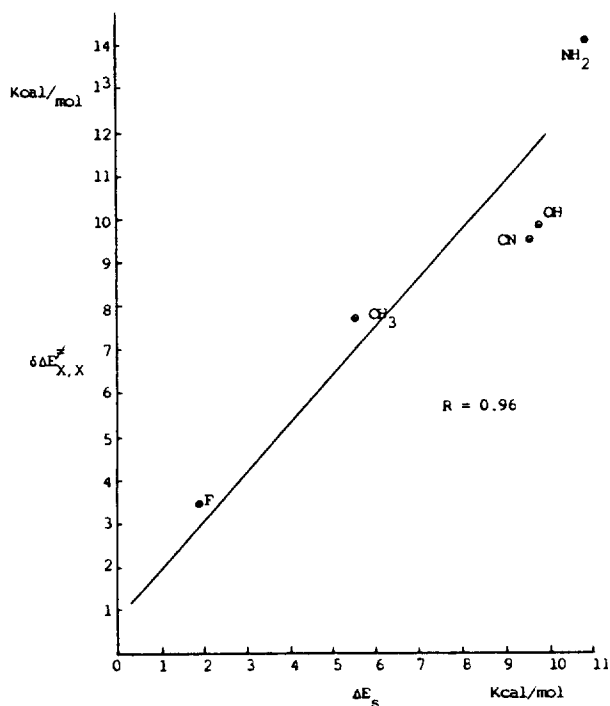


**Figure 4.** Plot of $\Delta E_s$ vs $\Delta E^*_s$.

**TABLE 3: Energy Barriers $\Delta E^*_{X,X}$, (for X = Y), Energies of Reaction, $\Delta E_{X,H}$, Radical Stabilization Energies of ·CH₂X, $\Delta E_s$, and Energy Barriers, $\Delta E^*_{X,H}$ (for X≠Y) (kcal/mol)**

| X | $\delta \Delta E^*_{X,X}$ | $\Delta E_{X,H}$ | $\Delta E^*_s$ | $\Delta E^*_{X,H}$ |
|---|---|---|---|---|
| H | 0.00 | 0.00 | 0.0 | 6.11 |
| F | 3.44 | 12.30 | 1.8 | 4.00 |
| CH₃ | 7.78 | 9.70 | 5.5 | 5.53 |
| CN | 9.39 | 12.10 | 9.5 | 5.34 |
| OH | 9.83 | 19.30 | 9.7 | 3.88 |
| NH₂ | 14.13 | 26.42 | 10.5 | 3.37 |

$^a\Delta E_s$ = BDE of C-H(X = H)-BDE of C-H(X≠H), and BDE of C-H(X = H) = 104.5 Kcal/mol. BDEs are averages of the values in (1) F.P. Lossing and J.L. Homes, *J. Am. Chem. Soc.*, **106**, 6917 (1984), and (2) J. Hine, "Structural Effect Equilibria in Org. Chem" p. 312. (Wiely, New York, 1975).

**TABLE 4: The C-H* Bond Length in the Reactant, $d$ and Transition State, $d^*$**

| X | $d^a$ | $d^{*a}$ | $\Delta d^b$ |
|---|---|---|---|
| H | 1.102 | 1.263 | 0.161 |
| F | 1.102 | 1.272 | 0.170 |
| CN | 1.111 | 1.294 | 0.183 |
| CH₃ | 1.111 | 1.293 | 0.182 |
| OH | 1.122 | 1.315 | 0.193 |
| NH₂ | 1.130 | 1.330 | 0.200 |

$^a$Å. $^b\Delta d = d^*-d$.

bination of two X atoms[20*] while B consists of three-electrc.. 2-$\sigma$ bond C---H---C. The overall system(A + B) resembles tetramethylene dianion(TMD) analog, the only difference being replacement of central C-C $\sigma$ bond in the TMD by the three-electron 2-$\sigma$ bond. However the latter bond is loose at the TS and hence will have a relatively low lying $\sigma^*$ orbital. Orbital interactions are expected only between orbitals of the same symmetry and hence three interactions, 1∼3, are possible between the two fragments. The interaction 1 between the two doubly occupied orbitals should be small being a second-order effect.[21] We would however expect the interaction 2 to be substantial since three-electron stabilization is involved and a net charge transfer to the fragment B from A should occur. The transfer of charge will however scarcely affect the length of C---H--- C since the orbital of the fragment B involved(SOMO) in the interaction 2 is a non-bonding type. The direct through-
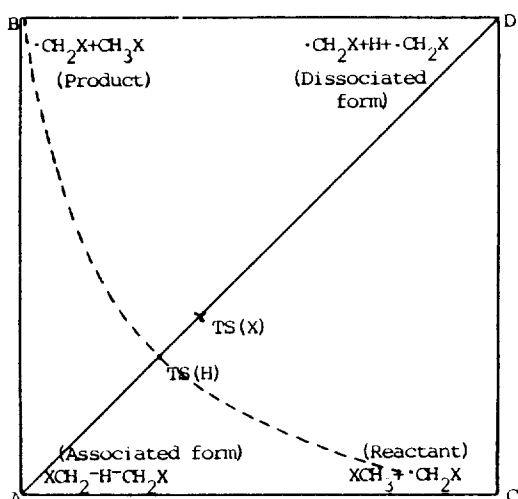


**Figure 5.** Variation of transition state with substituent X in the symmetric hydrogen atom transfer reaction.
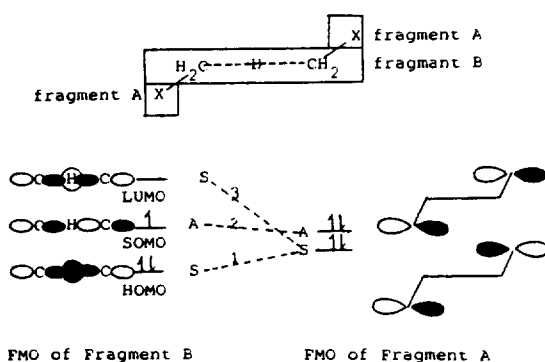


**Figure 6.** Orbital interaction scheme between the two fragments. Fragment A and B are formed by linear combination of two X atoms and by three-center three electron system, C---H---C, respectively. Frontier orbitals (FMO) only are considered. FMOs of the fragment A are symmetry adapted orbitals of the two nonbonding(n $\pm$) or pi($\pi \pm$) orbitals.

*Actual orbitals to be used in the orbital interaction between A and B are the symmetry adapted orbitals of the two nonbonding (n₁ and n₂) or (π₁ and π₂) orbitals. Since the distance between the two atoms is relatively great (2.52 A), direct interaction between the two orbitals will be small; energy splitting, $d\epsilon = \epsilon_+ - \epsilon_-$, will be small so that the two levels, n₊ and n₋, will be almost degenerate.

space interaction of the two nonbonding orbital on X atoms is out of question due to the long distance, 2.52 A, between the two atoms. This leaves only the final interaction 3 to be accounted for. This interaction 3 involves a doubly occupied and empty orbital, so that sizable charge transfer from A to B is conceivable. The charge transfer to the antibonding orbital(LUMO of B) will thus cause a significant increase in the bond length of C---H---C. According to the first order perturbation theory[22] the magnitude of the mixing coefficient $\alpha$ can be estimated using eq (2).

$$\alpha = \frac{H_{mn}}{\epsilon_m - \epsilon_n} = \frac{H_{mn}}{\Delta \epsilon} \qquad (2)$$

where $\epsilon_m$ and $\epsilon_n$ are energies of the two orbitals interacting and $H_{mn}$ is perturbation matrix element. Since it is difficult to estimate the magnitude of $H_{mn}$ qualitatively, we will consider only the effect of energy difference, $\Delta\epsilon$, between the HOMO $\epsilon^{HO}$ of the substituent X and the LUMO of the C---H---C bond. The $\epsilon_X^{HO}$ and $\Delta\epsilon$ values are summarized in Table 5. It can be seen in this Table that the $\Delta\epsilon$ is the largest, and hence $\alpha$ will be the smallest, for X = F, which is in agreement with the smallest change($\Delta d$) in the C-H* bond(Table 4) as expected from the least amount of charge transfer, while the $\Delta\epsilon$ is the smallest ($\alpha$ will be largest for X = NH₂, which is again consistent with the largest bond length change($\Delta d$), as expected from the greatest amount of charge transfer to the fragment B.

Finally we have applied the Marcus equation (3) to our data in Table 3.

$$\Delta E_{X,Y}^* = \frac{1}{2}(\Delta E_{X,X}^* + \Delta E_{Y,Y}^*) + \frac{1}{2}\Delta E$$
$$+ (\Delta E)^2/8(\Delta E_{X,X}^* + \Delta E_{Y,Y}^*) \qquad (3)$$

The equation relates the barrier height for the cross-reaction(X≠Y) of Y displacing X, $\Delta E_{X,Y}^*$, to the intrinsic bar-

**TABLE 5: The Highest Occupied MO(HOMO) of Substituents X and Energy gap $\Delta\epsilon$ Between the FMO's (Kcal/mol)**

| X | HOMO energy[a] level of X | $\Delta\epsilon$[b] |
|---|---|---|
| NH₂ | −11.10 | 15.20 |
| OH | −14.20 | 18.30 |
| F | −16.17 | 20.27 |
| CH₃ | −13.25 | 17.35 |
| CN | −12.30 | 16.40 |

[a] Obtained by averaging the MINDO/3-UHF HOMO levels of $\alpha$ and $\beta$ spin states of substituents X in the transition state. [b] The lowest unoccupied MO(LUMO) level of of CH₃---H---CH₃ is 4.10 Kcal/mol.

**TABLE 6: Energy Barriers for the Unsymmetrical Hydrogen Atom Transfer Reaction Obtained by MINDO/3($\Delta E_{X,Y}^*$) and by the Marcus Equation, ($\Delta E_{X,Y}^*$(Marcus)) (in Kcal/mol)**

| X | Y | $\Delta E_{X,Y}^*$(MINDO/3) | $\Delta E_{X,Y}$(Marcus) |
|---|---|---|---|
| H | F | 4.00 | 2.89 |
| H | OH | 3.88 | 3.49 |
| H | CH₃ | 5.53 | 5.74 |
| H | CN | 5.34 | 5.61 |
| H | NH₂ | 3.37 | 3.28 |
| F | CN | 13.76 | 12.51 |
| F | OH | 9.93 | 10.00 |
| NH₂ | CN | 10.97 | 11.47⁻ |

riers, $\Delta E^*_{X,X}$, and $\Delta E^*_{Y,Y}$, and the energy change, $\Delta E$. The $\Delta E^*_{X,Y}$ value obtained by MINDO/3 calculations and by the Marcus equation (3) are summarized in Table 6. The Marcus equation is seen to apply satisfactorily to the MINDO/3 results of energy barriers and energy change involved in the hydrogen atom transfer reaction.

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# Syntheses of Conjugated Dienes from 1–Alkenylboronic Acids by Palladium (II) Salt

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The reactions of (E)–1–hexenylboronic acid (1) or (E)–ß–phenylethenylboronic acid (2) with various olefins in acetonitrile at room temperature in the presence of lithium palladium chloride and triethylamine gave the corresponding (E, E)–conjugated dienes stereospecifically in good yields. (E)–ß–Phenylethenylboronic acid (2) was more reactive than (E)–1–hexenylboronic acid (1) in these vinylations. And these vinylations were also carried out catalytically when 10 mol % of lithium palladium chloride and cupric chloride, as the reoxidant of palladium, or 10 mol % of palladium acetate and mercuric acetate were added instead of stoichiometric amount of lithium palladium chloride.

## Introduction

The conjugated dienes are important intermediates in the syn-

thesis of a wide variety of compounds of value, as well as in their utilization in other reactions such as Diels–Alder reaction.[1] A number of methods for the preparation of conjugated